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Title: Progress in Self-healing Fiber-reinforced Polymer Composites

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Keywords: self-healing materials, fiber-reinforced polymer composites, damage, manufacturing, commercialization

Abstract

This paper sets out to review the current state-of-the-art in applying self-healing/self-repair to high performing advanced fiber-reinforced polymer composite materials (FRPs). A significant proportion of self-healing studies have focused so far on developing and assessing healing efficiency of bulk polymer systems, applied to particulate composites or low volume fraction fiber-reinforced materials. Only limited research has been undertaken on self-healing in advanced structural FRP composite materials. This review focuses on what has been achieved to date, the ongoing challenges which have arisen in implementing self-healing into FRPs, how considerations for industrialization and large scale manufacture must be considered from the outset, where self-healing may provide most benefits, and how a functionality like self-healing can be validated for application in real structures. Systems are compared in terms of process parameters, resulting mechanical properties, methods of healing assessment as well as values of healing quantification. Guidelines are further given for a concerted effort to drive towards standardization of tests, and the use of specific reinforcement architectures in order to allow reliable comparison between the available healing systems in structural composites.

Keywords: self-healing materials, fiber-reinforced polymer composites, damage, manufacturing, commercialization

1. Introduction

The intrinsically poor interlaminar properties of laminated fiber-reinforced polymers (FRPs) may lead to delamination and crack growth when subjected to flexural and compressive loading. This behavior has resulted in a reticence regarding their design, which led to their conservative use in real structures. This conservatism negates the potential weight-saving benefits that can be realized with fully optimized structures. With the potential for small-scale damage to grow or coalesce under subsequent loading, FRP structures incorporate high safety factors to account for this defect sensitivity to ensure they will remain load bearing throughout their service life. This paradigm has resulted in many research groups worldwide exploring and developing the concept of self-healing or self-repair being applied to FRPs, with the aim of achieving autonomous structural recovery via an embedded functionality, to address damage formation in its early stages before the integrity of the structure is compromised. In principle, this could reduce the structural redundancy, and fully realize the mass saving associated with using FRP composite materials.

This paper sets out to review the current state-of-the-art in applying self-healing/self-repair to high performing advanced fiber-reinforced polymer composite materials. Our definition of an advanced fiber-reinforced polymer composite material, for this work is as follows:

- A nominal fiber volume fraction, $V_f > 30\%$
- A nominal matrix modulus, $E > 500$ MPa

Our review will discuss what has been achieved to date, the ongoing challenges which have arisen in implementing self-healing into FRPs, how considerations for industrialization and large scale manufacture must be considered from the outset, where self-healing may provide

the most benefits (with respect to current FRP approaches to design), and how a functionality like self-healing can be validated for application in real structures.

A significant proportion of self-healing studies have focused on assessing the healing efficiency of the system in bulk polymers, liquid (or low fiber volume) polymers, particulate composites or low volume fraction fiber-reinforced materials with inferior mechanical properties.[1,2] Comparatively, limited research has been undertaken on self-healing in advanced FRP composite materials; specifically based on systems commonly used in industry, or those that possess high performance characteristics.

Two broad categories of self-healing systems can be found in the available literature:[3] (i) intrinsic self-healing systems, which can heal a crack through interactions (physical or chemical) at the molecular level; (ii) extrinsic self-healing systems, which utilize pre-embedded healing agents (via microcapsules or vascules) to fill the crack and reunite its faces, **Figure 1**. Section 2 reviews the main systems integrated so far into structural composites. It is worth making clear at this juncture that, to date, only repair of the polymer matrix has been demonstrated. If fibers are fractured, there is no remedial action available at this time. The integration of a self-healing/repair function within a high fiber volume fraction FRP presents some major challenges, as the embedded function must compete for volumetric space with the reinforcing fibers, **Figure 1.**

Naturally, the effectiveness of healing in composites is predicated on the question of how healing/recovery is characterized, which is discussed in section 3. Numerous methods to quantify healing performance have been reported, but a standard approach is yet to be decided. Currently, the variety of tests and performance metrics serves to hinder any direct comparisons and wider evaluation. Moreover, reported healing efficiencies often conflate

multiple strengthening or toughening mechanisms within FRPs, by the inclusion of entities such as microcapsules or vascules, or serve to diminish innate properties of the host structure due to the creation of defects, fiber architecture disruption, or alteration to load transfer capabilities.[4] Furthermore, any demonstrated loading scenarios must be representative and repeatable, and not serve to enhance the effectiveness of the healing agent.[5]

Any viable self-healing approach must be able to cope with the adverse environments to which it is exposed. This includes the processes encountered in manufacturing, as discussed in Section 4. In many cases, the underpinning chemistry behind the healing mechanism is either thermally activated or enhanced. In the small proportion of published research that investigates thermal stability, most inactive self-healing systems show a significant decrease in subsequent healing efficiency when exposed to temperatures above ambient.

Considering the process of manufacture in more general terms, incorporating an extrinsic additional functionality into an already highly architectured structure may affect the process as well as the quality of the produced composite. For example, achieving a dispersal of microcapsules, vascules and/or catalyst must be achieved in addition to the reinforcing fibers, which already typically occupy > 50% of the volume available, see Figure 1.[6–8] Furthermore, the presence of such secondary features can be detrimental to the manufacturing process e.g. compressibility and permeability of the fiber preform,[9] Figure 1. The challenges associated with incorporation of self-healing systems are evident in simple laboratory scale experiments: this is undoubtedly a factor in the slow progression of the technology to larger structures. However, it is quite apparent from a design perspective that imparting a self-healing functionality to an entire structure may not be necessary. Instead, specifically targeting critical

features and locations (such as joints, holes, edges and other discontinuities) may be a more viable and rewarding application of self-healing technologies, as discussed in section 5.

In most studies to date, the repair is not strictly autonomous; however, perhaps it is imprudent to consider non-autonomy as a barrier to maturation of the technology. Although fully autonomous self-healing capability is the long-term goal, current challenges in conventional repair of FRPs means that there is considerable value in developing and implementing an embedded repair function that still requires intervention or initiation. Indeed, the necessity for external intervention could be embraced as an opportunity to demonstrate a step-change in improving repair strategies that can be employed in FRP structures. At present, one of the most effective and commonly used FRP repair strategies is the use of externally bonded patches.[10] A self-healing system, which is competitive with such an approach in terms of either (i) the time required to effect the repair, (ii) repair effectiveness (in terms of operational lifetime, stiffness, strength or toughness), (iii) repair simplicity (e.g. simply heating the damaged area) or (iv) repair cost, could represent an achievable short-term target for existing self-healing technologies. Furthermore, manual intervention also presents a considerable advantage in terms of providing assurance and validation via inspection or monitoring; particularly where the application is safety critical or highly loaded. A major hurdle to the implementation of self-healing FRPs remains the challenge of manufacturing, characterization and validation: processing method, integration to the FRPs, performance, repeatability, monitoring, quality assurance. Such metrics are common barriers to the adoption of new technologies into commercial environments. Research is needed to demonstrate that self-healing functionality can remain effective for extended periods and in non-optimized, realistic environments; these aspects are evaluated in section 6.

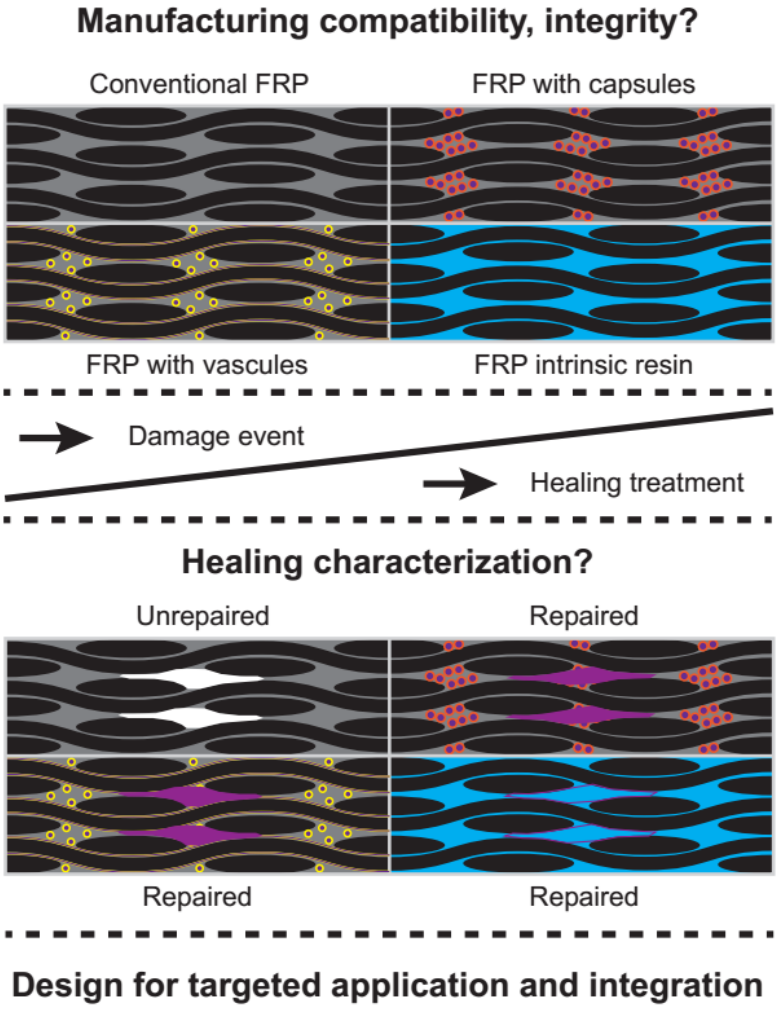

Figure 1: General concept to produce, test and design self-healing system within structural polymer composites (components not necessarily to scale).

2. Self-healing fiber-reinforced polymer composites: the state-of-the-art

Self-healing of polymeric materials has been extensively reviewed in recent years and the reader is directed to the following comprehensive articles describing systems, characterization and utilization of self-healing polymeric materials.[3,11–13] Much of this literature does not relate to or is not compatible with structural FRP composites. The following review adheres to our definition of what constitutes a FRP composite, as outlined in section 1, and highlights the

current state-of-the-art for self-healing and articulates what might be the future need to see its implementation at an industrial scale.

Self-healing polymeric materials are generally classified into two distinct groups, intrinsic and extrinsic (further classified as capsules and vascules), according to their method of incorporation. Those categories include further sub-categories, which are detailed with some examples in **Figure 2**. In practice, some systems blur the boundary between these groupings (notably thermoplastic-derived systems) and there are cases where both have been employed within one host structure. Indeed, there is an argument for doing the latter, since extrinsic and intrinsic approaches are complementary in terms of the length scales over which they are effective. The effect of healing (or recovery) performance is commonly described in terms of a healing efficiency (η). This dimensionless value has been defined in several ways, by multiple authors; however, it is most commonly expressed as a percentage in terms of strength, stiffness, or toughness and is typically derived in two forms:

$$\eta = 100 * [\frac{Healed\ property}{Pristine\ property}] \quad (1)$$

$$\eta = 100 * [\frac{Healed\ property - Damaged\ property}{Pristine\ property - Damaged\ property}] \quad (2)$$

For simplicity and because Equation 1 is derived from Equation 2 with the damaged property set to zero, Equation 2 is used exclusively in this article and where possible, published values reported herein have been modified for consistency. The nature of healing efficiency will be discussed in detail in section 3.

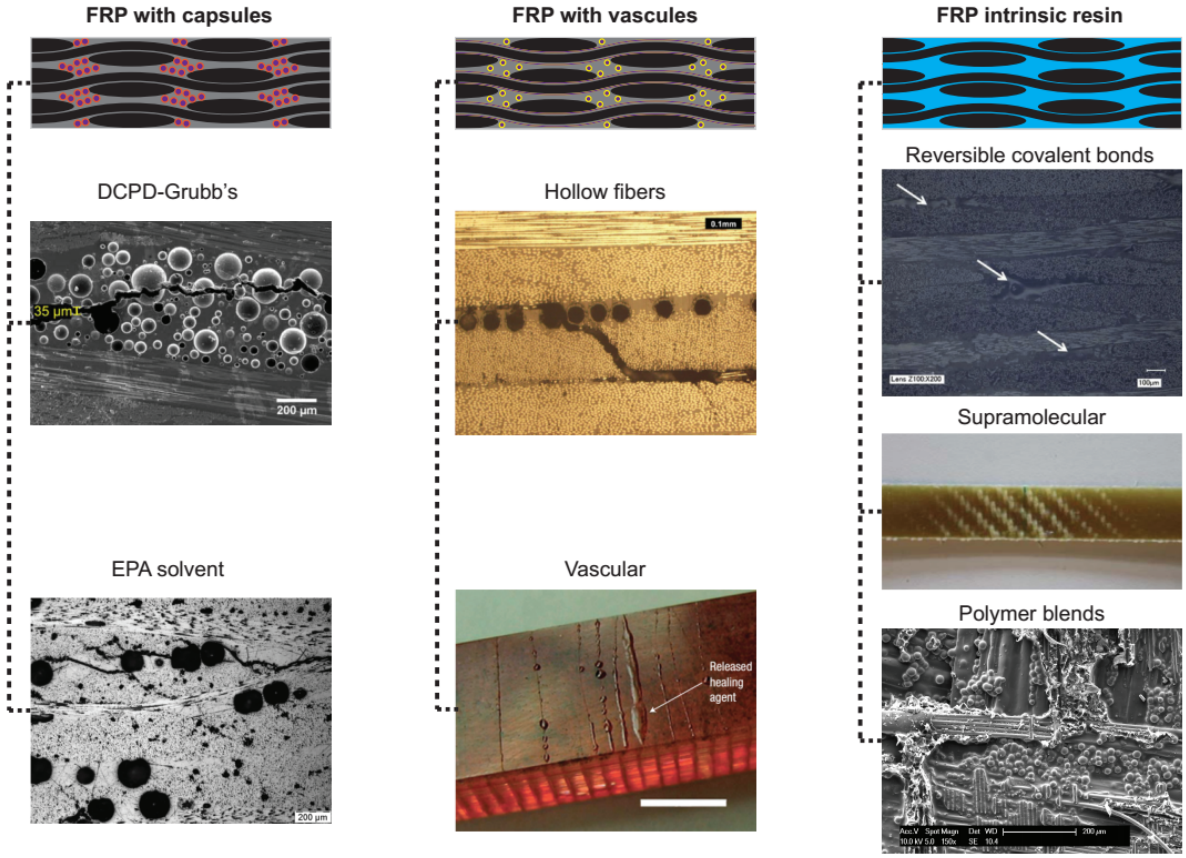

Figure 2: Classes of self-healing systems within structural polymer composites: (i) capsule-based systems including Dicyclopentadiene (DCPD)-Grubbs'[14] (Reproduced with permission.[14] Copyright 2010, Elsevier) and Ethyl phenyl acetate (EPA) solvent capsules;[15] (ii) vascular systems including hollow fibers[16] (Reproduced with permission.[16] Copyright 2007, Elsevier) and 3D vascular network (scale bar = 5 mm);[17] (Reproduced with permission.[17] Copyright 2007, Nature Publishing) (iii) intrinsic healing systems including reversible covalent bonds,[18] (Reproduced with permission.[18] Copyright 2017, Elsevier) Supramolecular resins[19] (Reproduced with permission.[19] Copyright 2017, IOP Publishing) and polymer blends.[20] (Reproduced with permission.[20] Copyright 2017, Elsevier)

2.1. Extrinsic self-healing

Extrinsic self-healing in FRPs is implemented by the inclusion of additional functional materials or architecture within the laminate. Upon damage formation, distributed microcapsules, which act as embedded healing agent reservoirs, or a network of microvascules, which form a circulatory network, are ruptured or breached, allowing the entrained liquid(s) to infuse the fracture surfaces. Following subsequent transformation of the liquid healing agent to a solid, structural integrity can be restored and the damage ameliorated.

Different approaches to incorporating extrinsic self-healing systems engender a range of advantages and disadvantages in terms of: damage volume, stoichiometry, repeated healing, gap filling, stability and long-term reactivity, host compatibility, ease of incorporation/manufacture, cost of constituents, and healing efficiency achievable.

2.1.1. Microencapsulation

This approach typically employs either a single or dual microcapsule archetype: the former predominantly relies upon activation post-release by a catalyst co-distributed throughout the matrix material to initiate cure; in the latter system, an appropriate hardener material is sequestered into separate capsules and also distributed throughout the matrix material, relying on mixing of the components to affect repair. Much of the seminal research exploited the Ring-Opening Metathesis Polymerization (ROMP) of dicyclopentadiene (DCPD) using Grubbs' catalyst. However, research was mainly limited to neat resin systems or where the matrix did not meet the selection criteria specified above, or where fiber volume was not reported or below the threshold amount.[1,21–27] Furthermore, the DCPD-Grubbs' system has several limitations such as deactivation during cure of the host matrix, dispersal, cost, toxicity and low temperature resistance. Although it has been shown that some of these concerns can be addressed by protecting the catalyst in a paraffin wax shell, doing so can have a significantly detrimental effect on the host material's mechanical properties.[2]

Patel et al.[28] incorporated the DCPD-Grubbs' system into woven glass-fiber-reinforced polymer composites (GFRPs) with the aim of improving compression after impact (CAI) strength. However, inclusion of the wax-encapsulated particles resulted in significantly longer crack lengths following impact than observed in control specimens. This could be attributed to matrix plasticization, or to the increased area/number of inclusions introduced, thus

reducing interlaminar mechanical properties. Although Patel et al.[28] report respectable healing efficiencies, these are inferred from the recovery of compressive strength (RCS) of the control panels containing microcapsules and wax particles (but no catalyst) which, as previously observed, increased delamination. Although the compressive strength of pristine non-functionalized laminates was reported, no RCS data at increasing impact energy levels was available for comparison; one has to be cautious therefore to consider if the improvement in RCS in healed specimens is only relative to the functionalized specimens with compromised damage resistance and therefore lower localized buckling loads of the sub-laminates. The exacerbation of damage due to inclusion of the wax particles may be less prominent at lower energy levels, thus facilitating higher true healing efficiency, but this needs to be investigated and reported if true healing efficiencies are to be established. Consistency, and validity, of calculating healing efficiency in a way that reflects the benefits of incorporating self-healings systems is discussed in section 3.

Yin et al. published a number of papers investigating the use of epoxy-loaded capsules with a copper complex as the embedded catalyst in FRP specimens.[29–32] Again, the fiber volume reported (27–30%) was lower than our selection criteria; however, the seminal nature of the research should not be overlooked and the reader is directed for further reading. Coope et al. investigated metal triflate based Lewis Acids as catalysts to circumvent the stability issues associated with Grubbs' catalyst but only demonstrated moderate healing capability in neat resin systems.[33]

Dual microcapsule systems facilitate separate integration of an epoxy healing agent and hardener, thus overcoming the issues associated with metal based catalysts such as cost, toxicity, reactivity, dispersal etc. Encapsulation of amine based curing agents is notoriously

difficult and requires more complex synthesis procedures and techniques than that required for encapsulation of epoxy materials, due to the difficulty in creating an amine suspension.[34,35] To circumvent the difficulties in stabilizing an amine suspension, attempts have been made to infiltrate hollow microcapsules and porous glass beads with an amine solution.[36–38] The latter method in particular enhanced the long term stability of the system even at elevated temperatures. Microfluidic devices have also been shown to successfully produce well controlled distributions of double emulsions using a photocurable middle phase to encapsulate an amine curing agent.[39,40] Alternative chemistries utilizing mercaptan, thiol, and imidazole based curing agents have also been successfully encapsulated and demonstrated in curing epoxies, but as with previous systems discussed, should be explored further to determine their capabilities in FRP samples.[41–43]

To the best of the authors' knowledge, very few single or double capsule systems have been demonstrated in FRPs that meet the selection criteria specified. One exception published by Bolimowski et al.[44] utilizes the same chemistry as Coope et al.[33], to functionalize unidirectional (UD) composite specimens. Although Bolimowski et al.[44] did not report fiber volume fraction, it can be inferred from the cure procedure reported, and the manufacturer's data, that the sample fiber volume should be between 52 and 56%. Double-cantilever beam (DCB) specimens demonstrated a maximum healing efficiency of 44% with a catalyst loading of 10 wt%; however, even this modest recovery is amplified by the significant detrimental effect the inclusion of the microcapsules and catalyst particles has on initial fracture toughness: the strain energy release rate of the virgin functionalized specimens only averaged 22% of that of the non-functionalized control specimens. Virgin fracture toughness inversely correlated with catalyst loading; however, decreasing catalyst loading resulted in lower healing efficiencies, presumably due to incomplete cure of the healing resin. Varying the

concentration of microcapsules was found to have no effect on healing efficiency, indicating the lowest concentration in the study provided sufficient resin to cover the fracture surface. Although it would be imprudent to draw conclusions about the validity of microcapsule/catalyst systems from a single study, and only based upon recovery of fracture toughness, it nevertheless raises questions about the effectiveness of this approach when employed in an FRP compared with a bulk polymer. It should also be noted that Bolimowski et al.[44] observed an average of 14% recovery in peak load in samples with no catalyst present, suggesting a significant contribution from the solvent induced polymer reptation between the host matrix and the healing agent, further questioning the effectiveness of the microcapsule/catalyst system.

Manfredi et al.[15,45] provided further insight into the effects of solvent inclusion and the disparity that exists between the performance of self-healing in bulk and fiber-reinforced polymers. Based upon previous work investigating solvent induced reptation for healing applications,[46–49] EPA microcapsules were dispersed onto dry woven glass fabrics before infusion via vacuum assisted resin infusion molding (VARIM, an industrially relevant manufacturing route), to produce samples with a nominal fiber volume fraction of 50%. However, the presence of the capsules reduced the compressive strength of virgin laminates by up to 53%, due to the attraction of propagating microcracks. Furthermore, no healing was observed in CAI testing. Several reasons were proposed: loss of healing agent due to processing and aging; unsuitability of the solvent for the resin system used; and the small scale over which polymer reptation acts to induce healing compared to the macroscopic parameters associated with CAI testing. The solvent microcapsules were also tested with respect to recovery of fracture toughness under Mode I loading.[45] However, no healing was observed, despite lightly clamping the fracture surfaces together to minimize interfacial

distance and ensure full wetting of the fracture surface. This is particularly noteworthy considering the complete recovery of stiffness achieved in the bulk polymer as reported previously.[50] Where DCB specimens were prepared by bonding two separate FRP plates with a functionalized intermediate layer of resin, healing efficiencies between 4–35% were achieved. When completely immersed, FRP samples exhibited an 80–95% lower uptake of EPA solvent compared to a fiber free polymer. This may be attributed to both the obvious lower relative volume of polymer present, but also the constraints imposed by the fibers on swelling, inhibiting the uptake of solvent. Since the main fracture mechanism of FRPs in Mode I loading is dominated by interfacial debonding during crack propagation, rather than propagation through matrix rich regions, it can be concluded that solvent based healing is not suitable in such domains (see **Figure 3**). Conversely however, solvent based healing may prove beneficial in areas that are typically resin rich, such as resin joints and areas with ply drops. However, healing imparted via entropic matrix swelling is reliant upon unreacted functionalities in the matrix. As the degree of cure can increase over time, healing efficiency decreases with aging time.[47,51]

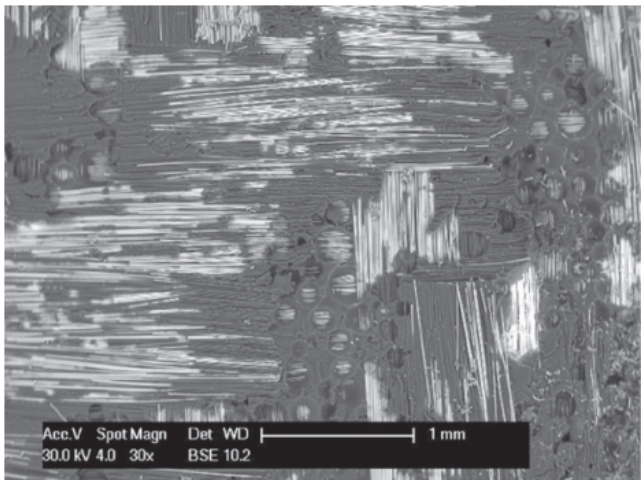

Figure 3: SEM image of the crack face of a healing specimen, showing traces of capsules and fiber bridging.[45] Reproduced with permission.[45] Copyright 2015, IOP Publishing.

The findings of Bolimowski et al.[44] and Manfredi et al.[15,45] hint at the disparate outcomes achieved when self-healing systems are applied to materials that either meet or fall short of the structural parameters defined at the outset. Future work needs to focus on the ability of self-healing to address the greater loading that will typically be imparted to high performance FRPs, which are not present in low fiber volume or bulk polymer materials.

2.1.2. Hollow-fiber systems

An alternative to the use of discrete microcapsules, and their inherent geometric incompatibility with a fibrous architecture, is to exploit the fibers themselves. The introduction of hollow fiber elements allows sequestration of healing agents within the fiber reinforcement. Damage events see the rupture of the hollow filaments, resulting in the release of the healing agents stored within. This allows adoption of similar healing agent approaches, as previously described for microencapsulation, where effusion of the entrained liquids can be undergo reaction (polymerization) to restore surrounding matrix integrity.[52] Note that although a variety of fiber materials have been considered, the majority of work has focused on hollow glass fibers (HGFs). Importantly, a modest number of such hollow fibers, dispersed amongst the conventional reinforcing filaments does not significantly degrade the global mechanical properties of the FRP.[53]

Bleay et al.[54] reported the first example of a HGF/epoxy FRP which demonstrated (non-autonomous) self-healing behavior. Continuous glass fibers of 15 μm outer and 5 μm inner diameter were impregnated with epoxy resin and cured into flat laminated panels containing hollow fibers orientated orthogonally. The hollow fibers within the laminate panels were then filled with healing agents; hardener in one fiber direction and epoxy in the other/s—both epoxy and hardener were diluted with acetone to facilitate this. This dilution was critical to

lower the healing agent viscosity to a sufficient level to enable its efficient release and distribution from the hollow fibres. This is of further note due to solvent-induced matrix swelling, which serves to increase the mobility of the surrounding polymer chains. The researchers then used compression after impact tests (CAI, 80 J) to quantify healing performance in terms of strength recovery. After a post-damage treatment of vacuum-assisted heating, modest strength recoveries of ca. 5% healing efficiency were achieved (in accordance with Equation 2). The researchers concluded that larger diameter fibers could help to increase the volume of healing agent availability and thus overall healing performance. However, this modest recovery may also be attributed to the high-energy nature of the impact; unrepairable fiber-damage may have occurred.

Accordingly, Pang and Bond[55,56] reported a similar hybrid HGF/solid E-glass fiber epoxy composite with comparatively large hollow fibers (60 μm external diameter, 50% hollowness). Using a resin film infusion process, pre-impregnated uncured tapes were prepared containing the hollow fibers. Similar to the work reported by Bleay et al.[54], the acetone-diluted epoxy healing agent was infused within the laminates post-cure. These researchers proposed an alternative method of healing quantification in terms of flexural strength recovery under four-point bending. To create a controlled damage region within the test specimens—and rupture the HGFs—a quasi-static indentation process was used to simulate low-energy impact, in contrast to the previous research. High energy impacts lead to fiber damage, which is not repairable by these recovery mechanisms. A 24-hour healing cycle under ambient conditions was employed in each case, following imparting of the damage. A healing efficiency of 73% was recorded; however, the research revealed a marked decrease in healing performance when the samples were stored for 3–9 weeks.

Trask and Bond[57] reported a similar system of hybrid solid/hollow glass fiber-reinforced epoxy. Interestingly, in attempt to maximize efficiency, the researchers conducted a study to identify the most critical interfaces with their specimens and positioned the healing fibers only at these positions. Again, damage was imparted using a quasi-static indentation method, **Figure 4**. However, in this work the researchers elected to use much shorter curing cycles, with test specimens subject to 100 °C for 2 hours before testing via four-point bending to ascertain flexural strength and stiffness. In contrast to previous work, some of these tested specimens were infused with healing agent prior to autoclave curing. On average, the healable laminates exhibited approximately 84% strength of the non-healable equivalents and were shown to recover 87% of the flexural strength of the undamaged non-healable baseline laminate.

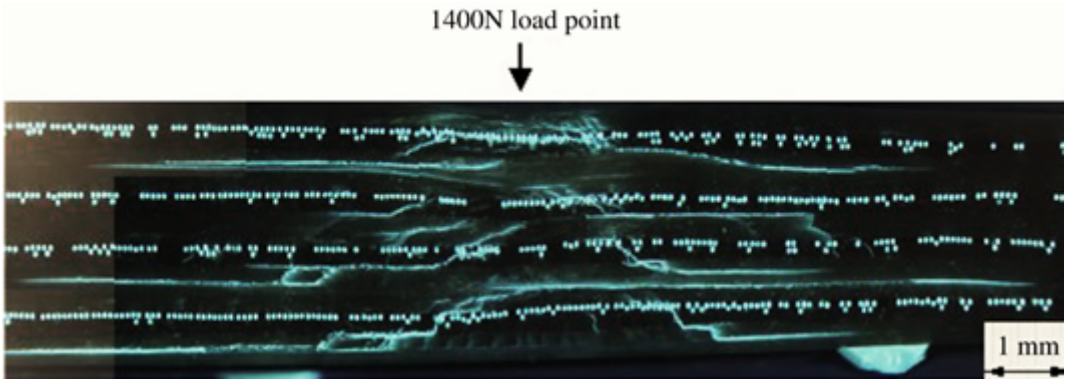

Figure 4: The release of UV-fluorescent 'healing agent' after pseudo impact damage.[57] Reproduced with permission.[57] Copyright 2005, IOP Publishing.

Williams et al.[6] reported the first example of a healable carbon-fiber-reinforced polymer (CFRP). In this article the researchers targeted the repair of a specific damage category which is frequently observed in FRP parts: barely-visible impact damage (BVID). HGFs were incorporated into two ply interfaces within a laminate of carbon fiber/epoxy and after cure, were infused with a pre-mixed two-part epoxy healing agent. Quasi-static indentation of peak loads 1.7 kN and 2.0 kN was used to simulate BVID in each specimen prior to healing (45

minutes at 70 °C, followed by 75 minutes at 125 °C) and being subject to four-point-bend flexural testing. Two different HGF distributions were investigated, **Figure 5**. Although the higher density of HGFs resulted in a greater degradation of baseline mechanical strength (8% reduction relative to unmodified CFRP, versus 2% for lower density), these specimens exhibited the best healing performance following the 2.0 kN indentation, reporting an 83% healing efficiency. This recovery represented a significant improvement in flexural strength relative to the damaged unmodified CFRP. The damage created by the 1.7 kN indentation was not sufficient to investigate recovery. Evidently, there is a limited window of damage in which it is practical to repair: too little damage where the recovery mechanism cannot be reliably initiated (and the recovery is inadequate compensation for the degradation of baseline performance), and too much damage, where irreparable fiber breakage occurs.

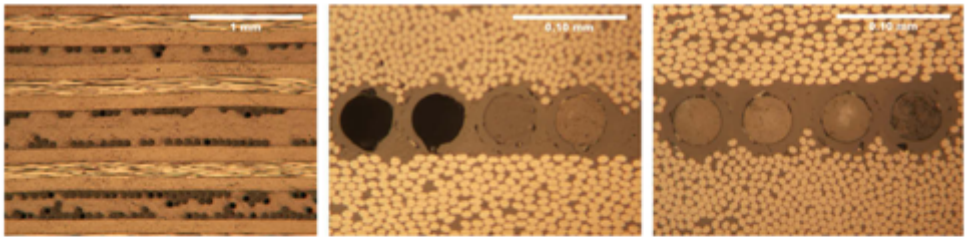

Figure 5: The distribution of HGFs throughout a carbon fiber laminate.[58] Reproduced with permission.[58] Copyright 2007, Elsevier.

Williams et al.[58] prepared in a subsequent study self-healing CFRP with embedded HGFs, as described previously. However, here the authors came back to the compression after impact method of assessing healing performance reported by Bleay et al.[54] This method was adjudged to be more representative of realistic damage and a more stringent assessment of healing performance (than flexural testing), due to the sensitivity of compressive strength to BVID. However, in contrast to the early CAI tests, these researchers used lower energy impacts (< 10 J), preventing significant fiber damage. The incorporation of HGFs at five

interfaces within CFRP test specimens saw a healing efficiency of 63%. The authors concluded that this hybrid system performed well, though conceded that the healing agent and method by which the HGF are infused, are far from ideal. In essence, at this point, meaningful recovery of realistic composite damage had been clearly demonstrated; however, this was limited by idealized cure-, manufacture-, and testing-environments.

Kousourakis and Mouritz[59] sought to expand understanding of the influence of HGF inclusion on the baseline mechanical performance of FRP laminates using a similar CFRP system to that reported by Williams et al.[58]. Studies were made of the influence of HGF diameter on the static stiffness, strength, toughness and fatigue performance of the host CFRP. These experiments were performed with empty HGFs, under the hypothesis that any entrained liquid healing agent would not significantly contribute to baseline mechanical performance. In stark contrast to the microcapsules discussed in section 2.1.1, this work concluded that there was little influence of HGF on stiffness or strength (compressive or tensile) when aligned with the load-bearing fibers (parallel to the loading force). Any small decrease could be attributed to a reduction in the overall volume fraction of higher performing fibers. In contrast, there is a small but significant degradation in both tensile and compressive strength (but not stiffness) with loading transverse to the HGF orientation for larger HGF diameters (ca. 200 μm). No significant influence on fatigue performance was noted from Mode I testing, though there was some improvement in toughness. A linear increase in G_{1C} (strain energy release rate) with respect to HGF diameter was observed. This effect was attributed to the HGFs acting as ‘crack stoppers’, pinning any cracks in place. The investigation into fatigue performance here serves to highlight its absence elsewhere, raising questions as to the viability of HGF healing over extended periods.

In contrast to some of the earlier work by Williams et al.[58] and Trask et al.[57], Kling et al.[60] reported an H-glass/epoxy GFRP in which all of the reinforcement fibers were hollow. Importantly, these HGFs were comparable in size to typical solid glass reinforcement, at approximately 10–12 μm outer diameter (ca. 50% hollowness). This FRP was cured into laminates via two methods, hand lay-up (HLU) and a vacuum assisted resin transfer molding (VARTM)-type process. After cure, the hollow fibers were filled with a catalyzed polyester healing agent (and accelerant). The healing performance was characterized via three-point bend flexural testing before and after impact damage, and a 12-hour 60 °C healing cycle. Recovery of flexural stiffness was observed for both VARTM and HLU prepared samples, although the HLU samples exhibited better recovery: healing efficiency of ca. 35%. This work concluded that the polyester healing agent was more robust than the epoxy agents reported previously, due to the former's insensitivity to mixing ratio (stoichiometry). The fiber-volume (reinforcement) fraction (V_f) was not reported, however, simple calculations using the laminate thickness and density suggest that the V_f is lower than the threshold set for this review. Nevertheless, this is a complex matter due to all of the fiber reinforcement being hollow. Consequently, the net density of the reinforcement is much lower than with typical glass fibers, although the ratio of fiber to matrix may be representative of a structural composite, the fiber volume fraction itself does not appear to be.

Zhu et al.[61] presented an alternative to glass-fiber encapsulation by preparing a woven E-glass epoxy composite (via HLU), which incorporated a healing-ply comprised of hollow polypropylene fibers (PP, filled with epoxy/mercaptan). To preserve the healing agent in the hollow fibers through the cure process, test laminates were cured at either 25 °C or 40 °C. The samples were then subject to the indentation method of simulating impact damage prior to healing at 70 °C for either 4 or 8 hours. Recovery was characterized using four-point bend

flexure. The novel healing agent represented a key part of this study: upon healing initiation, gas formation within the healing agent was intended to facilitate an internal pressurization, leading to its improved distribution across damaged areas. Impressive recoveries in flexural strength of up to 62% were reported for all specimen types containing healing agent.

Despite the success achieved by HGF-based healing systems in both carbon- and glass-fiber-reinforced plastics, several outstanding issues remain which have thus far prevented their uptake in industrial applications. The studies by Williams et al.[6,58] and Kousourakis and Mouritz[59] suggest that inclusion of HGFs parallel to load-bearing fibers does not severely degrade the baseline mechanical properties of the host laminate. Although there is a reduction in stiffness and strength transverse to the HGF direction, this is usually modest and may be adequately offset by an increase in toughness. In addition, it is worth noting that in many of the aforementioned cases, the fiber volume fraction was not reported. This makes it difficult to contextualize the quality of results: where the volume fractions are not representative of realistic high performance FRPs, the results have less relevance.

With a hollow-fiber approach, the most pressing challenges relate to the manufacturing complexity and the nature of the healing agent. Accordingly, researchers must consider: the position of the hollow-fibres (e.g. critical interfaces or uniformly distributed) and the method by which they are incorporated (e.g. as separate plies or otherwise); when the healing agent should be incorporated (e.g. pre-/post-cure); the extent of autonomy (e.g. thermally-initiated or ambient curing); the required volume of healing agent (i.e. V_f of the hollow fibers and their size/hollowness); healing agent viscosity (i.e. is it infusible) and stoichiometric mixing (where the agent is multi-component).

2.1.3. Vascular systems

A third method of effecting self-healing using an extrinsic approach is to utilize embedded vascular networks. Inspired by the transport networks found in both animals and plants, this approach uses networks of micro-channels, or vascules, to distribute and deliver healing agent to areas of damage. As for the two previous mechanisms, the principle relies on crack formation after a damage event propagating into an adjacent vascule. In turn, this rupturing then triggers the localized release of healing agent into the crack/s, initiating a repair.[62] This approach shares many similarities to that described for HGF, the primary difference being the replacement of discrete entities with a connected network. This difference has profound consequences on the associated methods of manufacture and the extent of reusability, since in principle vascules may be replenished to provide an ongoing healing capability.[17]

Williams et al.[63] developed a GFRP-skin/foam-core FRP sandwich panel capable of repair via a vascular network embedded within the foam core. A two-part low viscosity (<1000 cP) epoxy resin was chosen as the healing agent. Both syringes and a peristaltic pump were tested as a means of providing healing agent pressure which was delivered in either pre-mixed or as separate epoxy/hardener networks. Sandwich beam healing and general mechanical performance were assessed via edgewise compression (ASTM C364) after drop weight impact testing. All specimens were cured post-impact at ambient temperature for at least 48 hours, prior to a final 1 hour at 60 °C. Of the three categories of self-healing specimens tested, the ‘pre-mixed resin’ healing and the ‘high-pressure non-mixed’ healing performed well, with healing efficiencies of 143% and 150% respectively. This apparent increase above the virgin state can be rationalized in terms of the local densification of the damage foam core. The third category of healable specimens, ‘low-pressure non-mixed’, did not perform well, 39% healing efficiency. Post-test inspection revealed insufficient resin-hardener mixing and consequently a

failure of the healing agent to cure. This is a perennial challenge associated with multi-part agents. Moreover, this particular result serves as an important reminder that in almost all literature examples, systems that are intended to function 'autonomously' do not typically result in significant property recovery.

Norris et al.[8] prepared CFRP laminates incorporating a simple vascular array via a 'lost wax' process using low melting point solder which could be readily removed post-cure. The laminates were tested via compression after impact (low-velocity, 10 J), where the healing was achieved via infusion of epoxy resin through the network followed by a cure time of 7 days. Different vascule sizes and specimen configurations were tested, in all cases healing efficiencies of ca. 95% were observed. Evidently, useful recoveries were achievable using the vascular method; however, as with HGF systems, questions remained about the viability of manufacture and healing agent inclusion.

Presenting an alternative method of network manufacture, Patrick et al.[62] created microvascular networks via interweaving sacrificial Polylactic Acid (PLA) fibers (300 micron), infused with tin oxalate, into glass-fiber fabric preforms. The modified preforms were then infused using a VARTM process with epoxy resin and cured into laminates. When exposed to raised temperature (200–240 °C), the tin oxalate catalyzed a depolymerization of the PLA fibers to create a separate pair of embedded vascular networks. The researchers then investigated recovery in terms of delamination repair via DCB Mode I fracture toughness testing. During the fracture toughness testing, the dual networks of vascules were supplied with either hardener or epoxy. The crack was allowed to propagate until the rupture of the vasculature, after which point the specimens were unloaded and healing took place (48 hours at 30 °C). The specimens were reloaded and healed multiple

times, **Figure 6**. In both of the vascule morphologies tested, an increase in fracture toughness was reported after healing, when compared with the undamaged laminate. This was attributed to the improved toughness of the healing epoxy relative to the matrix epoxy. Increasing fracture toughness (in excess of 100% healing efficiency) was reported for consecutive healing events. Although excellent recovery was reported, it is certainly debatable if the 48-hour curing regime is viable. Clearly this would be dependent on the parts in which healing is desired.

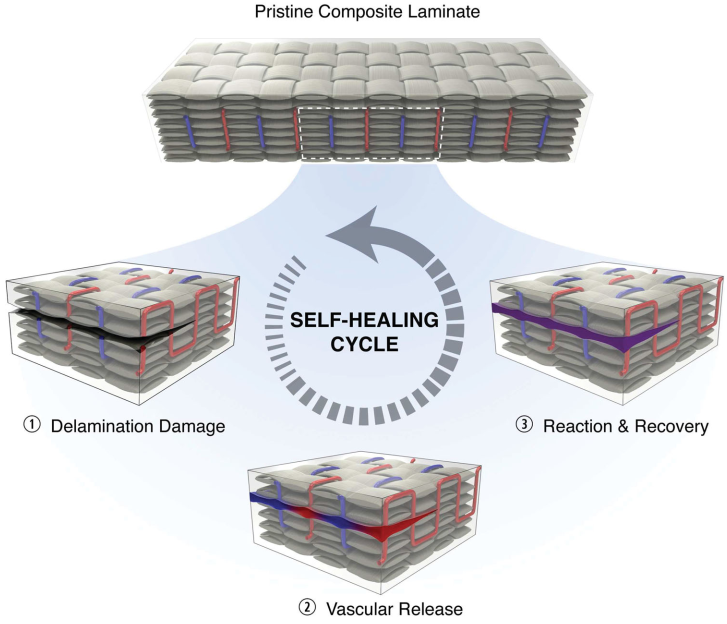

Figure 6: The delamination-repair cycle reported by Patrick et al.[62] Reproduced with permission.[62] Copyright 2014, Wiley.

The self-healing performance of cross-ply laminates after static and fatigue loading was investigated by Luterbacher et al.[64] In this study, a 1D vascular network was created via Polytetrafluoroethylene (PTFE)-coated nickel chromium wires (0.56 mm diameter). The wires were placed at discrete intervals during the lay-up, and removed after cure. The self-healing performance of the specimens was characterized in both static and fatigue (4 Hz) tensile testing. Two epoxies (RT151, Resintech, UK and an in-house formulation) were investigated

as healing agents by injecting in a pre-mixed form (to avoid stoichiometric limitations) with a syringe pump, after being subject to impact damage. The RT151 system was cured for 1 hour at 65 °C followed by 1 hour at 45 °C, the in-house epoxy was cured for 1 hour at 45 °C prior to a further 3 days under ambient conditions. In the static testing, there was no significant difference in stiffness or strength between the vascularized and baseline laminates. In the fatigue experiments there was some observed degradation in the stiffness of the vascularized specimens (compared to the baseline), this was more significant at high loading intensities. Static healing efficiencies (stiffness) were reported as 74% for RT151 and 67% for the in-house formulation. The difference being attributed to the lower viscosity of RT151, facilitating improved infusion into damaged regions. Under fatigue loading, stiffness was seen to decay by 7% over 50 000 cycles, which was initially fully recovered by healing, only to fail again within 2500 cycles of further loading. This relatively rapid degradation after healing is attributed to incomplete infusion and poor adhesion. This work further highlights the need for research into the dynamic performance of self-healing FRPs; good performance under static loading not necessarily being indicative of dynamic loading.

Despite the potential advantages of vascular networks over other healing mechanisms, their inclusion in FRPs tends to significantly complicate manufacturing. Moreover, the inclusion of 2D and 3D networks particularly disrupts fiber architecture, due to the presence of vasculature transverse to the fiber direction. The inclusion of such networks results in void formation and the presence of resin rich and resin poor pockets within the laminate. Vascule preforms also exert compression in adjacent plies up to a distance equivalent to six times the diameter of the vascule, affecting the stress field in the laminate when subject to load.[65] These factors contribute to a degradation in baseline mechanical performance which should be considered when assessing healing efficiency. In general, these effects can be mitigated by reducing the

diameter of the vasculature; however, this necessitates higher pressures to achieve equivalent healing efficiencies.[7]

Vascular healing has been demonstrated in structurally-relevant FRPs in a variety of ways. As for HGF healing, efficiencies close to (or in excess of) 100% are achievable. However, these studies usually consider highly idealized arrangements. The inclusion of a useful vasculature which does not significantly degrade baseline mechanical properties has been achieved, although none of these methods are fully optimized. Furthermore, excellent morphological control has also been demonstrated, and repeated healing of macroscale damage (delamination) within a structural FRP has also been achieved. Nevertheless, these achievements have not been made in any one single system, hence there are several challenges currently preventing the advancement of vascular healing as a concept. In terms of manufacture: rate and reliability should be considered, some of these methods are more suitable than others for scaling-up. There remain significant question marks over how healing agents are delivered in vascular systems: at present, manual pumping is required but this is unlikely to be feasible in many applications and further raises the question of autonomy. As with HGF and capsular systems, the nature of the healing is also important. No one agent has been optimized for extrinsic self-healing, though researchers should take care to consider viscosity, and the different practicalities associated with single- and multi-components systems. Ultimately, the nature of the healing agent is also critical in determining the healing regime; it is important to remember what conditions are achievable in service (i.e. are high temperatures and 24 hour cure cycles realistic?).

2.2. Intrinsic self-healing

Intrinsic self-healing systems are based on the intrinsic function of a polymeric material and offer the prospect of effecting repair via reversible bonding. These systems are often defined as 'mendable' polymers as many of the developed systems heal damage events under an external stimuli (typically heat).[66] In FRP applications, the development of intrinsic healing matrices can be divided into three main approaches: (i) systems based on the reversibility of covalent bonds; (ii) systems based on supramolecular interactions; (iii) systems based on polymer blends.

2.2.1. Reversible covalent bonds

The growth in use of thermoset matrices with or without fiber reinforcement for many applications, has highlighted the difficulty in repairing and/or recycling these covalently bonded, cross-linked systems. Sastri and Tesoro[67,68] introduced covalently bonded disulfide groups within an epoxy network which provided reversible crosslinks. These crosslinks could be activated upon heating while maintaining relatively high mechanical performance, notably in terms of stiffness (Young's modulus in the range of 20–200 MPa). These systems further demonstrated recovery of tensile strength in excess of 90% after a thermal treatment for 2 hours at 80 °C.[69] A recent study produced GFRP based on disulfide-containing organic-inorganic thermoset matrices with fiber volume fractions of about 50%.[18] A post-damage thermal treatment for 16 hours at 85 °C (with an applied pressure up to 20 bar), demonstrated full recovery of interlaminar fracture toughness and 80% recovery in strength after an 8 J impact. The application of high pressure throws into question the action of healing.

The selective thermal cleavage and reformation of (the same) covalent bonds represents a versatile strategy for repairing thermoset polymers and does so in a manner akin to

thermoplastic welding. Moreover, this strategy has been demonstrated in polymers which afford mechanical properties close to those of commercial epoxies and unsaturated polyesters. The most widely used reaction for these re-mendable systems is based on the Diels-Alder (DA) reaction, where a high density of crosslinks are generated by the reaction of electron-rich dienes (such as furans) and electron-poor dienophiles (typically maleimides). At temperatures above 120 °C, approximately 30% of monomer linkages disconnect, they then reconnect upon cooling to restore both the mechanical and visual properties (i.e. erase scratches) of the undamaged polymer. The first material utilizing this strategy was reported by Chen et al.[70] and showed recovery of 57% in terms of fracture load and of 41% in fracture toughness, as determined by compact tension tests after thermal mending at 120 °C. Furthermore, the researchers observed only a 20% reduction in the load to failure between the second and third healing cycles, showing the ability of these systems to heal repeatedly. However, these systems have a low temperature resistance (glass transition temperature is about 30–40 °C), which limits their application.[71] The chemistry and the wide variety of the different existing DA reaction systems was reviewed by Liu and Chuo[72] and Bergman and Wudl.[73] Park et al.[74] proved the utility of remendable DA matrices within FRPs. They processed a CFRP using this matrix and achieved a fiber volume fraction of 40%. They assessed damage healing efficiency through three-point bend flexural test and showed recovery in strain energy of around 90% in up to three successive damaging cycles when followed by a 150 °C resistive heating treatment. It is worth noting that in systems such as these, healing is performed above the glass transition temperature. Consequently, this method of repair may be inappropriate for some structures under residual loading, because this could cause a loss of structural integrity. Moreover, no quantification of the properties in the damaged state was performed. Importantly the hardness of these systems was comparable to

that of traditional Bisphenol A diglycidyl ether (DGEBA) epoxy resin (e.g. EPON 862 from Momentive). Heo and Sadano[75] successfully produced short-beam-shear specimens with a similar resin system to that of Chen et al.[70] using a VARTM process. Respective short beam strength healing efficiencies of 85% and 73% for the first and second healing cycles were demonstrated while keeping laminate mechanical performance in the range of conventional carbon fiber/epoxy systems.

2.2.2. Supramolecular interactions

In order to avoid a thermal trigger, systems based on non-covalent interactions have been developed.[76] However, these have resulted in relatively poor mechanical performance and are less appropriate for integration in FRPs. To overcome this issue, while keeping the healing process at ambient temperature (despite improved healing at higher temperatures), hybrid systems combining re-formable covalent and non-covalent bonds were developed.[77–79] Sordo et al.[79] observed that by combining bifunctional and tetrafunctional epoxy resins, the resulting polymer had the ability to fully recover (24 hours at ambient temperature) tensile properties after being cleaved. Sordo and Michaud[19] then demonstrated that these systems could be included within FRPs (with 50% fiber volume fraction) and could be produced using conventional manufacturing techniques. Moreover, after ambient temperature healing, recoveries of 65% and 72% of flexural strength and bending stiffness respectively were reported,[19] in addition to a recovery in impact force and dissipated energy of 55% and 76% respectively.[80] Even though these systems have shown high healing and damping properties, at present, the low stiffness of any resulting FRP limit their use to semi-structural applications.

2.2.3. *Polymer blends*

Self-healing via reversible covalent bonding has been shown to demonstrate efficient crack healing (section 2.2.1). However, the prerequisite to formulate completely new resin systems which exploit such chemistries is a major impediment to realizing self-healing in the near term. A self-healing strategy exploiting or adapting existing commercial resin systems is more readily applicable. Thus, the idea of thermoplastic blending, where a new thermoplastic phase is dispersed within a thermoset host, can lead to an ability for the thermoplastic phase to separate out under heating to facilitate crack healing. It is evidently disputable whether the application of temperature is technologically appropriate for providing crack healing on an in-service structural FRP. However, the systems are included here as they demonstrated large degrees of healing while keeping structural integrity during the healing treatment, as further detailed below.

Healing through the use of miscible polymer blends was demonstrated by Hayes et al.[81,82] where a solid-state epoxy resin was created by dissolving different weight fractions of thermoplastic (polybisphenol-A-co-epichlorohydrin) into epoxy resin (Epikote 828). Upon curing, the thermoplastic remained dissolved within the thermoset. After damage, healing could be achieved through heating at 130 °C, enabling the thermoplastic to diffuse through the thermoset and allowing chain re-entanglement at the crack faces. Results showed recovery in load to failure of these blended samples up to 70% with compact tension tests, and a recovery in Charpy impact energy of 50% for the blends containing the highest (20 wt%) thermoplastic content.[81,82] By tailoring the thermoplastic content as well as the healing temperature, recoveries of up to 66% in terms of reduction in damage area could be achieved after a 2.7 J impact, however, no mechanical recovery was quantified.

For immiscible thermoplastic/thermoset blends, the healing phenomenon is related to: (i) melting and subsequent volume expansion of the thermoplastic phase, (ii) flow of the melt into the damage volume, (iii) characteristic physical or chemical phenomena taking place at the molecular level.[83] This last mechanism can consist of either chain re-entanglement of the thermoplastic melt, based on thermally enhanced chain mobility, or the formation of reversible non-covalent (e.g. hydrogen or ionic) bonds in the thermoplastic phase. Two limiting morphologies are usually found, for healing purposes, depending on the constituent concentrations: (i) a particulate thermoset phase embedded in a thermoplastic matrix (e.g. [83,84]), obtained by polymerization-induced phase separation or (ii) a particulate thermoplastic phase embedded in a thermoset matrix (e.g. [85]), obtained by simple mixing of the thermoplastic material within the thermoset.

Systems consisting of a particulate thermoplastic phase embedded in a thermoset matrix have been studied for thermal healing applications in neat resins,[85,86] as well as when integrated into FRPs.[87,88] These studies mainly concern the ionomeric copolymer ethylene methacrylic acid (EMAA) blended with epoxy. The interest of this ionomeric copolymer resides in (i) the strong adhesion between epoxy and EMAA as covalent bonds are formed during curing[89] and (ii) the thermal expansion of EMAA that is seven times greater than that of epoxy.[85] Meure et al.[85] showed that by including 15 vol% EMAA particles within an epoxy resin, the strong adhesion between the two components increased the load to failure, measured by Mode I DCB crack opening, by up to 25%. After thermal healing of the cracked samples for 30 minutes at 150 °C, they further demonstrated recovery in fracture toughness of up to 85%. This amount of recovery was achieved thanks to the high expansibility of EMAA, which in addition creates gas bubbles during reaction with epoxy, creating pressure gradients which allow the EMAA to flow and fill the cracks. Those systems were further integrated into FRPs

made by hand lay-up,[87] which were characterized via Mode I DCB testing. This testing demonstrated, as compared to a relatively brittle epoxy composite, a 63% improvement in fracture toughness for EMAA-modified systems as well as the ability to recover this property by 156% after thermal healing thanks to the faculty of EMAA to expand and bridge the crack faces (see **Figure 7**). The potential of EMAA for thermal healing in FRPs has been further demonstrated when integrated in the form of layers[90] or stitches.[66] Even though those systems fully demonstrated the crack healing potential in damaged FRPs, EMAA is highly sensitive to humidity (data usually provided by manufacturers but no detailed research), which prohibits for now its application development.

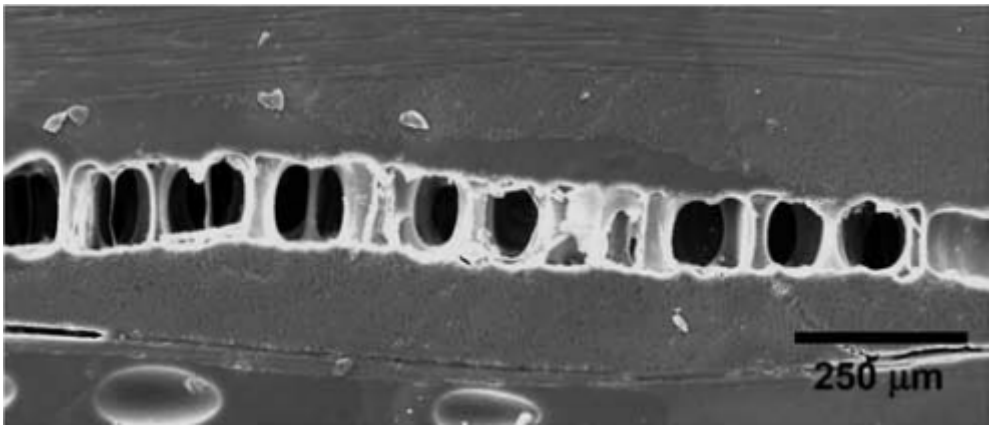

Figure 7: Delamination cracks in composites containing EMAA.[87] Reproduced with permission. [87] Copyright 2013, RSC Publishing.

Systems consisting of a particulate thermoset phase embedded in a thermoplastic matrix have also been studied for thermal healing applications in neat resins,[83,84] and when integrated into FRPs.[20,91] In these systems, the thermoset resin forms a network of interconnected particles, whose interstices contain a continuous thermoplastic phase having a significant self-diffusion (reptation) at moderate temperatures, but adequate thermal stability under service conditions. Luo et al.[84] first proposed creation of an epoxy-polycaprolactone (PCL) biphasic morphology containing 15.5 wt% PCL content in the matrix; the microstructure consisted of a

PCL matrix with particulate epoxy. Epoxy particles were thus interconnected and acted as "bricks" for load bearing, while the expansion of PCL (which expands at least 10 times more than epoxy at elevated temperatures) facilitates a differential expansive bleeding mechanism (comparable to EMAA blends). In a recent study, Cohades et al.[83] investigated a similar system, using lower healing temperature (150 °C, well below epoxy T_g of 200 °C; vs 190°C for Luo et al. [84]) in order to maintain structural integrity. Blends with 25 vol% PCL exhibited a healing efficiency in excess of 70%, while retaining suitable ambient-temperature mechanical properties ($E > 1.5$ GPa and $K_{IC} > 0.5$ MPa $m^{1/2}$) and were concluded to be promising candidates to be integrated as a matrix for healable FRPs. Woven E-glass FRPs with the epoxy-PCL blends were then manufactured through a VARIM process at high temperature.[20,91] The resulting laminate showed similar storage and bending modulus, bending strength and interfacial shear strength when compared to unmodified systems, however, toughness was decreased by 40%. After Mode I DCB testing, up to 45% toughness recovery and over 100% stiffness recovery were observed over several cycles when the blended matrix composite samples were re-tested after thermal mending.[20] Damage recovery after low-velocity impact was further assessed and composites with epoxy-PCL blends demonstrated similar energy absorption capacity to pure epoxy composites even though the extent of damage was higher. Ultimate compressive residual strength of the modified composites was 20 to 30% lower as compared to unmodified composites; however, these modified matrix composites were able to fully recover low-velocity impact damage after impacts of up to 8.5 J.[91]

3. Healing characterization

Due to their heterogeneous nature, FRP composite materials can lead to a multiplicity of failure modes depending on the intrinsic properties of the reinforcement and the matrix, but also on the interaction between these phases and thus their interfacial and interlaminar properties. This article focuses on composites with long fibers and thermoset matrices, thus delamination, intralaminar and translaminar fracture are the main matrix failure mechanisms, along with fiber fracture. In theory, damage repair (autonomous or via manual intervention) can recover any degraded matrix property following any type of damage. To quantify this recovery, the repair/healing efficiency concept was introduced and can be rewritten from section 2 as:[3]

$$\eta = \frac{f^{healed} - f^{damaged}}{f^{virgin} - f^{damaged}} \quad (3)$$

where f is the property of interest. However, caution must be taken when calculating healing efficiency:[15]

- $f^{damaged}$, the property in the damage state is often set to zero. This setting is true when measuring fracture properties in Mode I where the fracture resistance, after testing, is null. However, for other fracture modes and loading conditions, the property in the damage state is not null and thus needs to be measured;
- f^{virgin}, the property in the virgin state, can be that of the unmodified material (without healing system) or that of the modified material (with healing system). Indeed, the healing system usually influences the initial material properties and depending on which virgin property is used, the healing efficiency can be completely different. Thus considering both of these cases is of critical importance.

- f^{healed}, the property in the healed state can reach higher values than the property in the virgin state, in some cases. This is because many crack healing mechanisms create an interface of a new material and this material may have improved performance relative to the original matrix.

Section 2 provided a review of healing systems that were used to repair damage into structural FRP composites. These systems are compiled in **Table 1**, which defines the processes in terms of the same healing categories, whilst highlighting process parameters, resultant mechanical properties and the methods and values of healing assessment and quantification. The fiber volume fraction achieved is, in general, a function of the manufacturing method used, and is observed to vary substantially between the different studies. This parameter is a first indication of the extent of variability that is observed when comparing mechanical properties of different systems. This topic is further discussed in Section 4 below. Mechanical properties of the self-healing FRPs are reported in Table 1 in terms of a variety of metrics: First, strength, which is usually measured either in flexure or compression. This strength can be compared to the strength of a baseline FRP with the same reinforcement, but without healing functionality. Second, resistance to crack propagation (i.e. interlaminar fracture toughness) is also reported. This is typically compared to a baseline woven E-glass/epoxy laminate of interlaminar fracture toughness of 1000 J/m^2. Although stiffness (flexural, compressive and tensile) has been reported as a means of characterizing healing, Table 1 is limited to considering strength for simplicity, and because it is more representative of crack propagation and healing. Finally, the quantification method, the healing treatment and the reported healing efficiency are given in Table 1. Again, the diversity of tests and healing treatments prevent direct comparison between systems, consequently comparisons should be considered as only qualitative.

The recovery of mechanical properties in healable FRP composites has been measured via four main methods: Mode I crack opening, impact, compression after impact, and bending. Quasi-static fracture experiments (e.g. Mode I with the double cantilever beam (DCB) or the width-tapered double cantilever beam (WTDCB) geometries) are commonly performed when crack healing needs to be assessed directly, because they allow controlled and predictable crack propagation under tensile loading. Even though Mode I crack opening is convenient and provides controlled crack propagation, it implies large damage volumes which are not representative of realistic damage experienced by structural parts during service. Tests generating smaller damage volumes are thus of more practical interest in terms of industrial applicability. In contrast to Mode I experiments, low velocity impact testing is highly representative of in-service damage and has been extensively reviewed.[92,93] Low velocity impact damage is a critical concern in the aerospace sector where imperceptible damage events, attributed to operational or maintenance activities, can greatly decrease strength, durability and stability of the structure.[94] For example, in carbon-epoxy systems, BVID (arising from low velocity impact of blunt objects, typically 5-10 J) can lead to tensile and compressive strength losses of up to 50% and 60% respectively.[95] Higher-energy impacts can easily occur through such events, thus there is a significant interest in the autonomous healing of impact damage of up to 20 J. Healing efficiency can be quantified through this test in terms of recovery of impact force and absorbed energy, however, the obtained values were demonstrated to be only indicative of general trends (due to large statistical uncertainty).[18,80,91] A more common way to measure healing efficiency is to measure the recovery in impact damage area by means of optical or C-scan observations.[18,80,91]

Healing assessment in terms of strength recovery after impact damage can also be performed through the CAI test (i.e. measuring the recovery of compressive strength after impact).

Notice that Equation 3 is necessary to quantify healing efficiency in this case as the specimens are only 'partially damaged'.

Flexural testing is commonly used to measure flexural modulus and strength. In structural composites, these tests can be used to measure the flexural properties of specimens that have been previously impacted at a given energy. To quantify healing efficiency, this test requires again three states to be measured: the virgin state, the healed state and the damaged state.

Excluding quasi-static, Mode I fracture testing, healing efficiency quantification is typically performed after impact damage. The impact energies can vary between 1-80 J (see Table 1). Presently, all FRP self-healing systems have been developed to heal matrix damage only, i.e. no fiber damage. It is, therefore, debatable whether characterization of specimens that have been impacted at high energies, where fiber damage has been induced, is relevant or not.

Once damage has been created in a part, healing is not instantaneous. Healing treatments vary in nature, but all depend on three critical parameters: time, temperature and pressure. Generally, as the value of these parameters increases, healing is observed to be more effective. Again, it is disputable whether the application of temperature and pressure is technologically appropriate for providing crack healing on an in-service structural FRP. While pressure is complicated to apply to in-service parts, localized heating can be comparatively easily applied to damaged regions. Although thermal resolution is poor in general because of the facile conduction of heat, the relatively poor thermal conductivity of common FRP matrices enables reasonably good spatial control. The use of elevated temperature to induce/improve repair needs to be carefully considered. Heating must be assessed for compatibility with the material's thermal transitions as some healing temperatures can be above the matrix T_g and thus could compromise structural integrity. However, the thermal

repair of an unloaded structure, assuming sufficient spatial control, should be possible without structural compromise. Finally, even with fully autonomous systems (where repair is effected without heat, pressure or any other additional stimulus), the duration of repair must also be considered; in many cases it may be of greater technological concern to leave a part to heal for several days at ambient, than to apply raised temperature.

Table 1 shows the maximum healing efficiency for each reported study. This has been recalculated from the data provided in the corresponding publications, in accordance with Equation 3. As some data were taken directly from graphical representations, there may be a discrepancy between values originally reported and those recalculated herein. As expected from the variation seen with fiber volume fractions, mechanical properties and assessment methods, the reported healing efficiencies vary substantially. However, these values are a function of the damage volume to be healed, which is typically a function of the impact energy imparted to the object (see **Figure 8**). As a general trend, for each healing system, healing efficiency decreases as the impact energy increases. This is because delamination becomes more important, but also because above a critical threshold fiber rupture is initiated. The rate at which the efficiency decreases when impact energy is increased differs for each system due to various parameters, and cannot be readily identified from Figure 8 as work is usually only reported at one impact energy. In that respect, two studies reported healing efficiency values for three different impact energies,[18,91] and the tendency for the repair system to be less efficient as damage increases was confirmed accordingly, but the rate of this decrease was not consistent. A second representation of healing efficiency values is given in **Figure 9** as a function of the strength of the healing FRP in the undamaged state normalized by the strength of a baseline (provided in each reported study, without any healing functionality). For the case of intrinsic systems, these reference materials simply employ a

commercially available thermosetting polymer matrix. This comparison shows that a maximum level of healing can be reached in all healing systems (assessed as a function of the damage volume, see Figure 8). However, the normalized strength leads to a sharp divergence between intrinsic and extrinsic systems. Even though extrinsic healing systems can be quite intrusive, a tailored insertion (as has been studied by many research groups) provides strength values close to baseline systems, which is not the case for intrinsic, where new resin formulations are necessitated and consequently it is more difficult to reach the strength of commercial systems. Note that the solvent filled microcapsule systems of Manfredi et al.[96] are not linked to extrinsic systems in Figure 9 due to their non-healing behavior.

Obviously, the comparison of the different healing systems found for structural FRP composites in the available literature reveals that small damage volumes can be fully healed. However, the reliability of further comparison is questioned because of: (i) the multicomponent nature (reinforcement, matrix, interface, healing system) and (ii) the many different tests used to characterize healing. Now that self-healing is increasingly studied in the literature, there is a need for a concerted effort to drive towards standardization of testing, and the use of specific reinforcement architectures in order to allow reliable comparison between the available healing systems in structural FRP composites—both in terms of the initial and the recovered properties (i.e. healing capability). Such an effort has been made to quantify the healing efficiency of thermoset polymers;[97] however, structural composites have an additional dimension of complexity where the variation in reinforcement type, architecture, and stacking sequence, all complicate the overall comparison. This natural complexity of FRPs means that it is of paramount importance to not further complicate analysis. Consequently, some form of standardization, or at least uniformity in the reinforcements and testing methods is necessary. Self-healing systems have been broadly designed to repair

microcracks, and tests which characterize healing need to be designed to impart appropriate levels of damage to the specimens to reflect this. The Mode I DCB test is certainly a useful tool in many cases for measuring the interlaminar fracture toughness of composite laminates; however, it induces large damage volume relative to the specimen dimensions. Therefore, to prevent this, specimens need to be clamped to provide smaller damage volumes and thus test predetermined levels of healing. This clamping procedure is not representative of what would occur in real-life structures. Thus, mode I DCB testing needs to be complemented by testing which investigates response to impact damage, and allow healing of representative damage volumes. Through impact testing, the extent of specimen damage can be readily varied (by the impact energy used) and thus the range of healing effectiveness can be quantified. Evidently, there is no one perfect solution, without a consensus of the materials community, to the question of which reinforcement and standardized test to use in order to characterize healing. However, the authors suggest that new studies in this field should, at the first instance, model their experiments on established studies (in terms of reinforcement, techniques and conditions) in order to facilitate comparison with at least one existing system. Also, if impact testing is to be adopted, the above discussion leads to the recommendation that several impact energies should be used in order to test different extents of damage. An attempt to reliably compare three different systems was reported for the intrinsic healing of composites.[18,80,91] In these studies, similar impact energies, reinforcements, architecture and ply stacking sequences were used. These investigations, combined with the fact that in two of these studies[18,91] three different damage volumes (impact energies) were assessed, allowed a fairer comparison and thus yielded a more reliable conclusion of the effectiveness of those systems. Note that even though Mode I DCB tests were first used to prove the efficacy of the materials, they extended

the characterization to impact damage in order to obtain damage representative of real life structures.[18,20,91]

Table 1: Self-healing structural composites: mechanical properties and healing efficiency. Values indicated with * were recalculated from data provided into the reference

	Healing agent	Type of matrix	Type of Reinforcement	Process method	V_f [%]	Strength [MPa]	Strength Baseline [MPa]	Toughness	Healing assessment	Healing treatment	Healing efficiency [%]	Ref.
Microcapsules	DCPD-Grubbs'	Epon 828	Plain Weave Carbon fiber	HLU, compression	37.5*			2.79-2.85 [MPa $m^{1/2}$]	WTDCB	RT for 48h 80°C for 48h	38% 66%	[26]
	DCPD-Grubbs'	Epon 862	plain weave S2-glass fabric	HLU, compression	33	82 (compression)	80 (compression)		CAI at 45.1 J	RT for 48h, 1077 kPa	68% 78%	[28]
	DCPD-Grubbs'	Epon 862	Plain weave E-glass	HLU, compression	36				Indentation	Overnight at 30°C	100%	[98]
	EPA solvent	Epon 828	Weave 2x2 E-glass	VARIM	54	160 (compression)	260 (compression)	796.8 J/m^2	Mode I DCB	1-5 d at RT	0%	[45]
Hollow Fibers	Epoxy	Epoxy	HGF (Hollex)	Prepreg					CAI at 80 J	60 °C for 1h	5%*	[54]
	MY750 epoxy	Epoxy	Hybrid HGF/E-glass fibers	Prepreg	61.5	624 (bending)	668 (bending)		4PBT after ≈0.5 J impact	24h at RT	73%*	[56]
	Cycom 823	Epoxy	Hybrid HGF/E-glass fibers	Prepreg	57	559 (bending)	668 (bending)		4PBT after ≈0.6 J impact	2h at 100°C	129%*	[57]
	Discrete HGF	Epoxy	Hexcel T300/914	Prepreg	60	535 (bending)	583 (bending)		4PBT after ≈0.7 J impact	70°C, 125°C	83.2%*	[6]
	Discrete HGF	Epoxy	Hexcel T300/914	Prepreg	60	373 (compression)	330 (compression)		CAI at 3 J	70°C, 125°C	62.6%*	[58]
	Discrete HGF	Epoxy	Hexcel T300/914	Prepreg	60	580 (compression)	610 (compression)	600-800 J/m^2				[59]
	Discrete HGF	Epoxy	H-glass weave reinforcement	VARTM	25.1*	270 (bending)			3PBT after impact at 9.3 J	RT for 120h	19.3%*	[60]
	H(PP)F	Epon 828	Woven E-glass	HLU	41	500 (bending)	530 (bending)		4PBT after ≈0.5 J impact	RT	62%*	[61]
Vascular	Epoxy	913 Epoxy	E-glass (Hexcel)	Prepreg	58	184 (compression)			CAI at 3J	RT, 60°C for 1h	40%*	[63]
	Epoxy with EPA	Epoxy	Hexcel IM7/8552	Prepreg	58	350-370 (compression)	390 (compression)	1000 J/m^2	CAI at 10 J	RT for 7 days	96-99%	[8]
	Epoxy	Epoxy	8H satin weave E-glass	VARTM	20.5*			480 J/m^2	Mode I DCB	30°C 48h	90%	[62]
	Epoxy or blend	Epoxy	E-glass (Hexcel)	Prepreg	57	462 (tensile)	471 (tensile)		Static tensile testing at 15 kN	1h at 45-65°C, RT 3 days	67-74%*	[64]
Reversible covalent bonds	Disulphide thermoset	Same as healing	Weave 2x2 E-glass fabric	VARIM	51	75 (bending)	389 (bending)	650 J/m^2	Visual after 8.5 J impact	16h at 85°C with 0.2 bar	85.3%	[18]
	Mendomer (DA rx)	Same as healing	AS4 carbon fibers	Pressure holding	40				Recovery in strain energy	150°C for 1min	92-94%	[74]
	Polyurethanes (DA rx)	Same as healing	Unidirectional carbon fabric	VARTM		55.7 (short beam)	65.2 (short beam)		SBS	6.9 bar, 135, 90, 70°C	87.8%	[75]
Supra mol	Reverlink HR-NR	Same as healing	Weave 2x2 E-glass	VARIM	48.9	33.5 (bending)	389 (bending)		Visual after 20 J impact	28 days at RT	100%	[19,80]
Polymer Blends	polybisphenol	Epon 828	Cross-ply E-glass	VARIM					Visual after 2.7 J impact	130°C for 1h	30%	[81,82]
	EMAA	Epoxy	Plain weave carbon	HLU	52			410 J/m^2	Mode I DCB	150°C 30min	156%	[66,87]
	PCL	Epon 828	Weave 2x2 E-glass	VARIM	48	349.9 (bending)	389 (bending)	620.3 J/m^2	Visual after 8.5 J impact	150°C 30min	94.9%	[20,91]

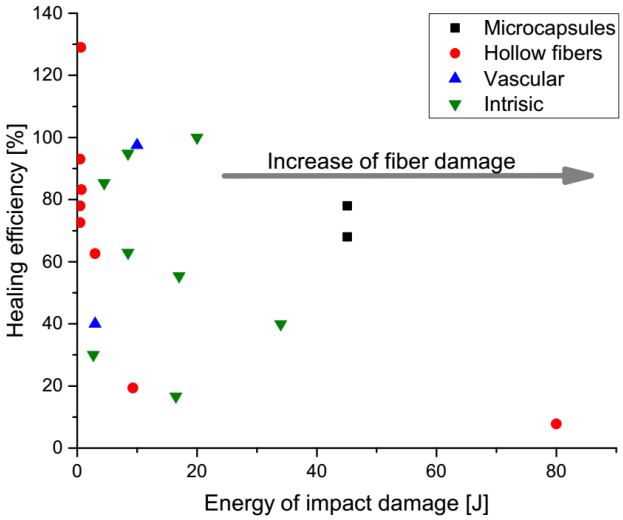

Figure 8: Healing efficiency as a function of the impact energy used to provide damage, for the studies reported in Table 1. Some studies provided additional healing data, which has been included here.

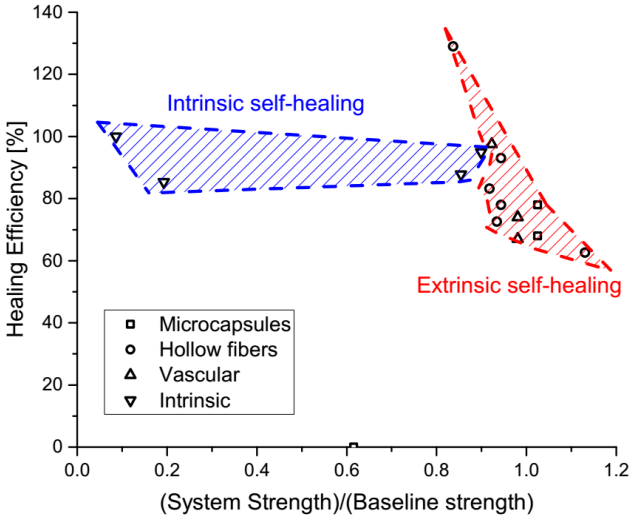

Figure 9: Performance map of self-healing structural composites, from data provided in Table 1. Maximum healing efficiency is shown as a function of system strength normalized by the baseline strength (i.e. without healing functionality). Data are divided as Intrinsic or Extrinsic, and further subdivided as: Microcapsules, Hollow Fibers, Vascular and Intrinsic.

4. Manufacturing compatibility

As reported in the previous section, high volume fraction fiber composites are considered herein; thus any potential healing system or matrix will have to be compatible with the geometrical and physical requirements linked with composite processing practices. When considering thermoset composite processing, a few methods are currently economically viable for generic parts (depending on the desired volume of production): hand lay-up, liquid composite molding techniques (vacuum infusion, resin transfer molding), molding of pre-impregnated fabrics or of prepreg materials under vacuum only or under pressure imposed by gas (autoclave) or by a press, and finally automated tape lay-up or placement. These are schematically presented in **Figure 10**. In addition, the reinforcement can be under the form of unidirectional plies or non-crimp fabrics, or of textiles.[99]

When integrating extrinsic healing systems with FRPs, the architecture of the reinforcement is of critical importance. Indeed, woven reinforcements have been used in many healing studies, rather than unidirectional arrays, because resin rich areas are found between crossing warp and fill yarns where the capsules can be naturally stored without affecting the intrinsic waviness of the fiber reinforcement, if their size is lower than the resin rich gaps.[28] The introduction of extrinsic systems, which have a dimension comparable to or larger than the natural void space in the reinforcement will generate distortions, and in turn modify the achievable V_f as well as initial (mostly compressive and interlaminar, as well as fatigue) properties.[9,16,45,100–104]

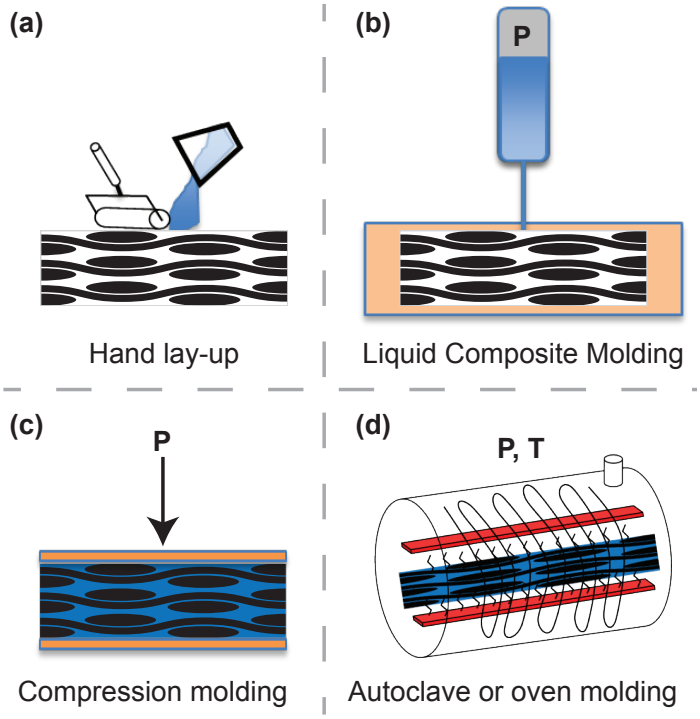

Figure 10: Schematic description of fiber-reinforced composite processing techniques.(a) is a manual process whereby resin is forced by a compaction roller into the reinforcement, (b) is an infiltration process whereby liquid resin is forced to flow (under pressure or vacuum or both) into the reinforcement held within a mold (rigid, or with a flexible top), (c) is a consolidation process whereby pre-impregnated reinforcement is pressed in a closing mold, and (d) is a process whereby a pre-impregnated reinforcement is sealed under vacuum, then consolidated and cured in an oven or an autoclave. Automated tape lay-up or placement is not shown here, but consists in robotic placement of pre-impregnated reinforcement tapes followed by consolidation as in (c) or (d).

In addition, processing must be adapted to ensure that the capsules or hollow fibers do not rupture during part manufacturing. This is a major limitation of these extrinsic systems for their application to high volume fraction fiber composites. In general, low-pressure consolidation techniques are required, so as to preserve the microcapsules or hollow fibers from breaking during processing. As an example, in the work of Manfredi et al.,[45,100] urea-formaldehyde capsules, which were shown to rupture under a force of 4 to 6 mN could be successfully introduced into glass fiber composites (with fiber volume fractions around 40%) only with an adapted VARIM process, with 0.3 bars as pressure difference, instead of a full vacuum as usually employed. The microcapsules used for self-healing studies in FRPs were typically of 200 µm diameter, which is around 20 times larger than single glass or carbon fibers (8-16 µm). The thickness of the stacks of plies is therefore increased, which results in a

decrease of the fiber volume content and of virgin interlaminar fracture toughness. As these microcapsules may have a toughening effect (by crack arrest), a compromise can be found to maintain similar interlaminar properties to non-healable FRPs. Another route would be to vary the aspect ratio of the spherical particles in order to keep the same volume of liquid healing agent, while keeping the same FRP thickness. Recent work[9] also showed that a compromise can be found by an adapted match of the capsule dimensions and the textile microstructure, allowing capsules to nest without deforming the structure too much. Nonetheless, scale-up possibilities remain limited, also considering that capsule production is so far often proposed in laboratory scale batch process, although scale-up can be envisaged using continuous parallel microfluidics lines, or techniques borrowed from industrial microcapsule production, as found in laundry detergents.

Systems relying on the introduction of fugitive vascular systems are somewhat more easily adapted, as they are well integrated into the reinforcement and can sustain higher compaction pressure. As a result, vascular systems and hollow fibers are in general more compatible with unidirectional reinforcements (as often used with pre-impregnated plies), as long as they align well with the fiber direction, in a similar fashion as integrated optical fiber networks.[105,106]

Concerning the resin properties, in general, the resin needs to flow a certain amount, in particular in liquid composite molding processes. For intrinsic systems, the resin viscosity is usually higher than that of conventional resins and flow is thus limited, leading to slower processes, or to the need for higher processing temperature. For extrinsic systems containing microcapsules, the viscosity of the polymer is greatly increased if the capsules are mixed into the flowing polymer; aggregation of the particles might severely limit the flow of liquid through the reinforcement. One solution to this problem, which does not change the resin

permeability (and can even increase it), is to functionalize the reinforcement prior to infusion as demonstrated by Manfredi et al.[100] However, in that case, the choice of epoxy resin system remains limited to resins with relatively low cure temperature, so as to remain within the stability range of the capsules (in terms of capsule shell stability and breaking strength above room temperature). In general, room temperature or low cure temperature (around 35 °C) are selected to demonstrate the principle.

Experimental studies reported above often rely on a hand lay-up manufacturing techniques to process FRPs. However, this process leads to low fiber volume content (usually 30%) as well as the high void content of the final part. Mechanical properties in the virgin state may therefore be lower than expected for a structural composite; as a result, healing assessment may be biased. Higher reinforcement contents and improved quality are obtained using vacuum infusion, as reported in[18,19,80,91] for example. Although the host FRPs investigated thus far have typically been prepared via simple hand lay-up or infusion techniques, several additional techniques have been utilized to incorporate the self-healing functionality.[8,18,20,45,55,64,98,107–109] Autoclave compaction of pre-impregnated plies has also been explored with capsules, as reported in Bolimowski et al.[44] Adaptation in the cure and post-cure temperature may however be required. As an example, for microencapsulated healing systems, the temperature needs to be carefully chosen to avoid damaging the microcapsules, whereas in latent functionality systems, appropriate cure schedules need to be defined in order to achieve the right amount of latent functionality.

Overall, all processes are in principle applicable as long as pressure and temperature are tailored to the healing system, and as long as the size of healing reservoirs is compatible with the porosity of the reinforcement network, which is sometimes difficult to achieve. Many of

the self-healing embodiments or chemistries still cannot readily be scaled and/or are incompatible with industrial processing techniques such as autoclave cure, resin transfer molding, automated tape lay-up or automated fiber placement. These incompatibilities may be attributed to a variety of factors, the main ones remaining the geometrical, thermal and mechanical constraints imposed by the reinforcement and the process requirements.

5. Self-healing by design: targeted applications

To date, the pursuit of self-healing FRPs has focused almost exclusively on laboratory or small-scale studies, investigating uniform and regular coupons, with few examples of attempts to work at the larger scale.[90,110,111] Furthermore, it has generally been the case that workers have sought to confer a self-healing capability as a ubiquitous function throughout the entire FRP host. While this could result in a fully self-healing material, as has been shown above, it raises questions of manufacturability, cost and performance. While this approach has served its purpose most effectively, it has perhaps missed an opportunity to demonstrate self-healing FRPs as a solution to specific complex and difficult loading or damage scenarios, often very localized as a result of design, and thereby justify the further investment in their realization.

For example, skin-stiffened FRP panel structures are widely used for lightweight applications in aerospace, and increasingly finding applications in other sectors; marine, automotive, renewable energy. For a variety of reasons, such as access holes or changes in section or loading, stringers have to be terminated. These so called “stringer run-outs” are sensitive to localized damage initiation as the loads from the stringer end have to be transferred into the skin, leading to the need for localized design solutions or the use of additional fasteners to assure fail safe design criteria can be met.[112] Upon excessive loading, the stringer tends to

delaminate at the skin-stringer interface and then delaminations propagate into the skin. This mechanism has been described and covered by several authors.[113–116]

Other examples of local design features where self-healing may offer benefits include, T-joints, changes in panel/section thickness (ply drops), holes (either for access or for fasteners), adhesive joints, and free edges, **Figure 11**.[10,117] By their nature, all of these design features can give rise to damage cases as a result of their in-service loading. This raises the prospect of "design for self-healing' where consideration can be given to the inclusion of self-healing functionality from the outset, as a means of avoiding implementation of more complex or less satisfactory remedial measures e.g. mechanical fasteners, Z-pinning.[118]

The judicious selection, combination and tailoring of the various intrinsic and extrinsic self-healing approaches, to address the likely type and extent of damage morphologies commonly associated with such practical design features, provides an opportunity to demonstrate the value and capability of self-healing within FRPs. Furthermore, the inherent manufacturing techniques, necessary for the creation of these design features, provide opportunities to incorporate self-healing functionality without major detriment or disruption to the host structure e.g. microcapsule inclusion in void region associated with ply drop, vascular network localized to edges of access/fastener hole.

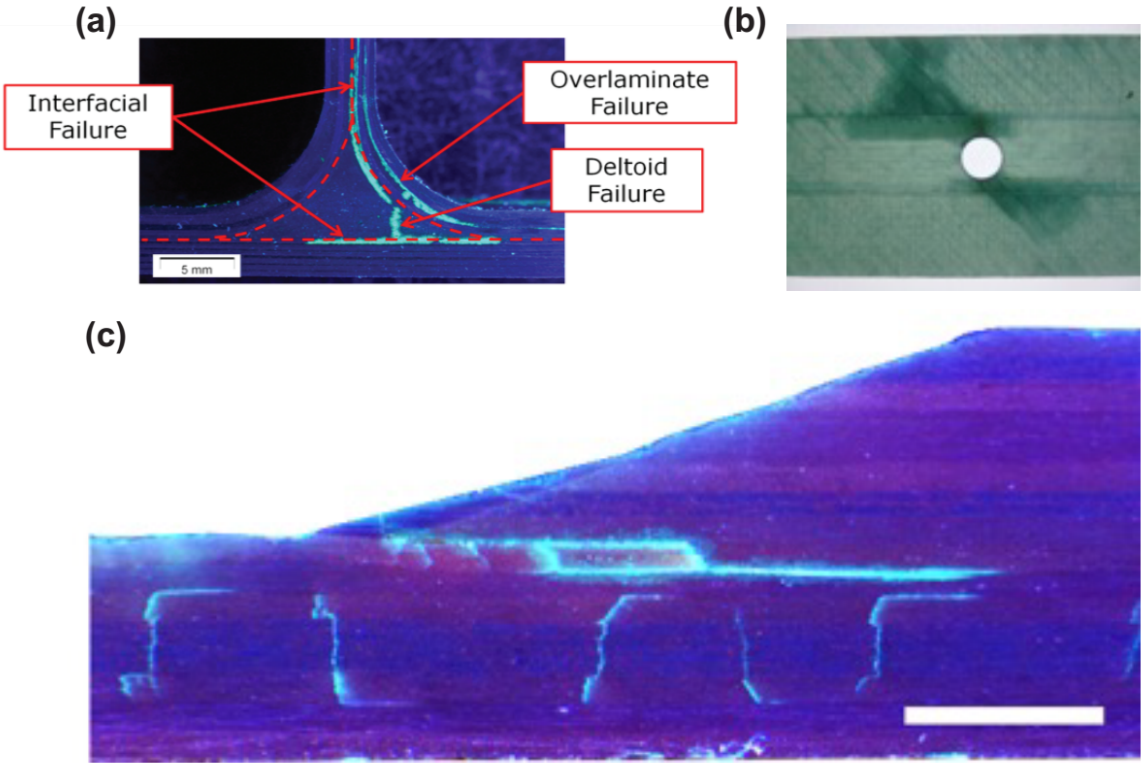

Figure 11: Typical localized design features suitable for targeted application of self-healing FRPs; (a) T-joint, (b) open hole, (c) stringer run-out (scale bar = 1 mm).

6. Validation

To find application in commercial products, self-healing FRPs must be trusted by both the original manufacturers and end users. Broadly, this confidence in their ability to perform reliably and repeatedly is a product of validation. Hereafter we define validation as evidence that the technology works, is robust and reliable, and is demonstrable via inspection. In much of the literature, including most of the state-of-the-art presented herein, the work has successfully proven that the technology can recover some degree of structural performance. Whether this has been demonstrated to an extent that means the technology is cost-effective is another matter. Regardless, in most of the examples given, the work has not proven that the technology is robust and/or reliable. With the advent of a new technology, proof of concept is paramount, whereas reliability and robustness are secondary considerations. However, it is

now suggested that in order for self-healing technologies to progress to the next stage of development, it is perhaps time to initiate research to address these concerns.

Evidently, validation is intimately related to the nature by which recovery is quantified (see section 3). After an initial period of testing under laboratory optimized conditions, further work needs to consider more realistic load cases (both static and dynamic), the effect of environment (pressure/temperature/humidity) and the effect of extended service/longevity. The ability to validate self-healing (either in its latent potency or final completion) by non-destructive methods is urgently needed to avoid the current test to destruction approaches. Computational science, in the context of structural fiber-reinforced composites, may also bring large improvements in the validation of such systems for a potential implementation, as has been seen with self-healing ceramic matrix composites for example,[119] but has not been deeply studied for self-healing FRPs yet. The combination of self-healing with a sensory network to create a responsive form of structural health monitoring (SHM) has been proposed; however, this is likely to compromise the goal of autonomy currently sought. Perhaps more simply, one might imagine an extrinsic self-healing system which uses an electromagnetically active healing agent. Upon release/cure of the agent, the electromagnetic profile would locally change around the damaged area. Regular inspection during routine maintenance would thus reveal the action of the healing mechanism. Techniques for embedded sensing associated with SHM have been the focus of a considerable amount of research, one of the most developed techniques is described by the research of Kirkby who has used optical fibers to detect the occurrence of impact damage.[120] It is very likely that only a self-healing functionality in an FRP which can be uncompromisingly validated will only attract the confidence of both manufacturers and end-users.

7. Conclusion

Although numerous self-healing systems have been tested in FRPs, there remain no examples of their industrial/commercial application. In this report, a multitude of factors have been identified that have contributed to this lack of commercialization, some factors are common to all self-healing systems, whereas others are system specific. The specific advantages and perhaps more pertinently, disadvantages, of each self-healing category are detailed in Table 2.

Table 2: The system-specific advantages and limitations of self-healing categories, note that healing efficiencies approaching (or exceeding) 100% have been reported for each category as seen in Table 1. Note that more general limitations which apply to all (or almost all) self-healing systems are not tabulated but are discussed below.

Self-healing system	Advantages	Disadvantages/limitations
Microcapsules	Autonomous activation has been demonstrated	Increases manufacturing complexity
	Catalyst activation eliminates requirement for stoichiometric mixing of healing agent	Moderate reinforcement disruption: significant degradation of baseline mechanical performance
		Limited damage volumes
		Single use at any one location, with residual voidage after rupture
		Dual capsules: stoichiometric mixing required
		Healing agent leakage
		Challenging encapsulation and dispersion
Hollow-fibers	Little degradation of baseline mechanical properties	Increases manufacturing complexity
	Moderate healing volumes	Limited reuse
	Autonomous activation has been demonstrated	Dual fibers: stoichiometric mixing required
		Healing agent inclusion is challenging
Vascules	Large healing volumes	Severely increases manufacturing complexity
	Extensive reusability	Limited autonomy (manual pumping of healing agents)
	External reservoirs of healing agent reduce stability issues	2D/3D networks can significantly degrade baseline mechanical performance
	Pressurized delivery promotes mixing	Dual networks: stoichiometric mixing required (remains poor even when pressurized)
	Hydrodynamic shielding of crack tips	
Intrinsic	Extensive reusability	Very small healing volumes
	Comparatively simple (conventional) manufacturing	Requires intimate contact of crack faces
	Non-intrusive: does not deform fiber architecture	Can severely degrade baseline mechanical performance (compared to traditional matrices)

Further to the system-specific limitations addressed in Table 2, are more general considerations which apply in almost all cases of self-healing composites. In general, the majority of self-healing studies—even those citing structural composites as a target application—do not involve the testing of FRPs, which are structurally useful. I.e. self-healing

is infrequently tested in materials which approximate the mechanical performance of industrially relevant materials. A vast number of healing chemistries and architectures have been investigated, but more focus is required on researching the implications of self-healing in composites rather than developing new systems which have not been optimized for such usage.

Very few studies have addressed the performance of aged (healable) composites or even their fatigue response. In the few studies which have led such investigations, healing performance has been observed to significantly deteriorate with time.[55,64] More of these investigations are required, as is analysis of the root cause of the instability: only by investigating this phenomenon can effective solutions be proposed.

Similarly, few systems have demonstrated fully autonomous healing and those that have usually suffer from low healing efficiencies. In multi-component (extrinsic) systems this is often due to incomplete cure of the healing agent, which in turn is a product of poor mixing and/or uneven reagent distributions. Overall, in both intrinsic and extrinsic classes, heat is usually required to affect a repair within practicable timescales. This is true of the vast majority of successful systems and immediately characterizes them as semi-autonomous at best. However, the suggestion from this report is that semi-autonomous healing is, at present, a much more achievable target than fully-autonomous healing and importantly may be just as industrially relevant.

As illustrated by Table 1, there exists a variety of ways to characterize recovery and calculate healing efficiency. However, there is a clear need to test self-healing composites in less-idealized conditions, and with more standardized and representative tests. This will lead to a more objective analysis of ‘healing performance’. The key recommendation from the analysis

in this article is that future research should consider using impact-based experiments to characterize healing at the first instance. This is primarily due to these tests being more representative of realistic damage states. Furthermore, to most effectively characterize recovery, at least three different impact energies should be used: healing efficiency tends to be inversely proportional to the extent of damage. Evidently, the sensitivity of this relationship is a metric which deserves attention.

In general, the field of self-healing is plagued by the complications it imparts on manufacturing. In composites this is compounded by the variety and complexity of processing methods. For all cases, the temperature should be carefully controlled during manufacture to strike a balance between the optimized mechanical performance of the host composite and the optimized healing performance of the embedded functionality. In the case of intrinsic systems this means controlling the temperature to retain enough latent functionality. In the case of extrinsic systems, this means curing the composite but not curing the healing agent (during manufacture). For vascular (and hollow-fiber) systems the healing agent can be added after cure; however, in doing so the overall manufacture may be greatly complicated. Consequently, it is necessary to assess the viability of doing this for the specific application in mind. If these systems are to progress, considerable optimization of their manufacture is required. Ultimately, as out-of-autoclave processes mature (e.g. resin transfer molding, compression molding and automated tape lay-up) researchers should consider attempting to incorporate their systems with these methods (which are all readily automated).

One of the most important conclusions from this article is that in the short-term, self-healing is unlikely to be viable when incorporated throughout complete composite structures. Although this may represent a desirable long-term goal, in reality self-healing is most likely to

be financially viable when used selectively in critical locations within critical parts: consequently, researchers should consider targeted application. At its simplest, this may take the form of identifying where self-healing can offer greatest value.

Few self-healing studies have discussed the subject of validation, but due to the nature of this technology, self-healing is unlikely to be employed in commercial materials without consumer confidence and reliable validation methods. Therefore, it is critically important that this is considered when developing healing systems, old and new alike. Combining self-healing with structural health monitoring may present one solution to this.

Although self-healing technology has greatly advanced in recent years, there is yet much research to come before self-healing composites will be found within the structures of cars, aircraft, watercraft or wind turbines. To take the next steps towards commercialization, the target applications of self-healing composites as well as their means of manufacture, characterization and validation will all require careful consideration.

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